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(§) Process for producing a thin-walled tubing from a zirconium-niobium alloy.

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(7) Proprietor: WESTINGHOUSE ELECTRIC CORPORATION
Westinghouse Building Gateway Center Pittsburgh Pennsylvania 15235 (US)

(7) Inventor: Sabol, George Paul 37 Morris Street Export Pennsylvania (US) Inventor: McDonald III, Samuel Gilbert 1339 Foxboro Drive Monroeville Pennsylvania (US)

(A) Representative: van Berlyn, Ronald Gilbert 23, Centre Heights London, NW3 6JG (GB)

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Description

This invention relates to a process for fabricating thin-walled tubing such as nuclear fuel cladding, from a zirconium-niobium alloy such that the alloys of the resultant products have a particular microstructure which enables the material to resist corrosion in high temperature aqueous environments.

Binary zirconium-niobium (Zr-Nb) alloys have been traditionally of interest to the nuclear industry because of their high strengths. It is this feature, in conjuction with reasonably good corrosion resistance, which ultimately led to the selection of the alloy of zirconium containing 2.5 per cent by weight niobium, as the standard pressure tube material for present generation Canadian Deuterium Uranium (CANDU) reactors. Although it was orginally believed that the zirconium-niobium alloys had inferior resistance to irradiation enhanced corrosion relative to existing alloys, such as Zircaloy-2 or Zircaloy-4, it ultimately became apparent that they actually had superior in-pile corrosion properties when properly heat treated, as described by J. E. LeSurf, ASTM STP—458, p. 286. As a result of this finding, there has been increasing interest in zirconium-niobium alloys as potential fuel cladding materials in future generation, high performance, light water reactors.

At present, there is one major drawback which could prevent successful employment of zirconium-nloblum alloys as fuel cladding materials. This problem stems from the fact that superior corrosion resistance has been obtained only after application of the following multi-step processing sequence: 1) anneal at 850—950°C and water quench; 2) cold work to 10 to 30 per cent reduction (optional); and 3) anneal for approximately 24 hours at approximately 500°C. This processing is easily applied to the thick-walled pressure tubes for which it was developed, but cannot be applied to commercially produced thin-walled tubing with its inherently tight dimensional specifications and long lengths (~4 m), which causes problems relative to maintaining the shape of the tubing. It is thus necessary that an alternate processing system be adopted for the production of thin walled tubing from zirconium-niobium alloys, for use as fuel cladding. Also, any such processing system must yield superior corrosion resistance and at the same time, be consistent with practices employed in the commercial production of fuel cladding.

We have found that zirconium-nioblum alloys can be fabricated into thin-walled tubing, of about 1.106 mm (0.040 inch) or less in wall thickness, which exhibits excellent corrosion resistance, by a process that does not require extensively long final annealing times, by the use of relatively low temperature anneals between cold working steps and a final low temperature anneal. By using the processing techniques of the present invention, thin-walled tubing can be fabricated that has a microstructure where second phase betaniobium particles are homogeneously dispersed in the zirconium matrix in extremely fine particle size to provide excellent corrosion resistance of the resultant article under both in-pile and out-of-pile conditions.

Accordingly, the present invention resides in a process for fabricating thin-walled tubing having a wall thickness of about 1 mm or less from a zirconium-niobium alloy containing from 1 to 2.5 per cent by weight niobium as homogeneously dispersed finely divided particles and optlonally up to 0.5% by weight of Cu, Fe, Mo, Ni, W, V or Cr as a third element, balance, apart from impurities, zirconium, characterized by betatreating a zirconium-niobium alloy billet containing from 1 to 2.5 per cent by weight niobium; extruding said beta-treated billet at a temperature no higher than 650°C to form a tube shell; further deforming said tube shell by cold working the same in a plurality of cold working stages; annealing said tube shell, between each of said stages of cold working, at a temperature below 650°C; and final annealing the resultant tubing at a temperature below 600°C, so as to produce a microstructure of the material having nlobium particles of a size below about 800 angstroms (80 nm) homogeneously dispersed therein.

The fabrication of thin-walled tubing from a zirconium-niobium alloy is effected according to the present invention with the production of tubing exhibiting excellent corrosion resistance and resistance to hydride formation.

Especially useful are zirconium alloys containing 1.0 per cent by weight and 2.5 per cent by weight niobium. The zirconium-niobium alloys may contain a minor amount, up to 0.5 per cent by welght of a third element, such as copper, iron, molybdenum, nickel, tungsten, vanadium and chromium. An example of such an alloy is one containing zirconium with 2.5 per cent niobium and 0.5 per cent copper.

In one embodiment of the invention, the alloys are first subjected to a beta-treatment by heating the alloy to form 950—1000°C and water-quenching the same to a temperature below the alpha + beta to alpha transus temperature. The billet is then prepared for extrusion by drilling an axlal hole along the centre line of the billet, machining the outside diametre to desired dimensions, and applying a lubricant to the surfaces of the billet. the billet diameter is then reduced by extrusion at a lower than covnentional temperature, below 700°C, through a frustoconical die and over a mandrel. A beta-anneal of the extruded tube shell may then be effected, depending upon the alloy, by heating to form 850—1050°C, followed by rapid cooling. The billet may then be cold worked by pilgering, at a source of primary fabrication, to reduce the wall thickness and outside diameter. This intermediate production is called a TREX (Tube Reduced Extrusion), which may then be sent to a tube mill for fabrication by cold working, intermediate low temperature annealing, and a final anneal under the fabricating steps of the present invention to produce the desired thin-walled tubing. In the formation of the thin-walled tubing, the material is preferably cold worked by pilgering, and 3 to 5 stages of cold working effected, preferably 3 to 4 stages.

The present invention produces thin-walled zirconium alloy tubing wherein the alloying elements are 65 homogeneously dispersed throughout the zirconium in a finely divided state. The particles,

homogeneously dispersed are of an average particle size below 800 angstroms (80 nm) and preferably the average particle size is below about 500 angstroms (50 nm).

In order that the invention can be more clearly understood, convenient embodiments thereof will now be described, by way of example, with reference to the accompanying drawings in which:

Figure 1 is a flow diagram of a process for fabricating thin-walled tubing;

Figure 2 is a graph illustrating the superior corrosion resistance of the zirconium-niobium alloy containing 1 per cent niobium processed according to the flow diagram of Figure 1, as compared with reported corrosion resistance of such an alloy;

Figures 3A, B, C and D show transmission electron microscopy photomicrographs illustrating the typical precipitate distribution and size observed in a fully annealed tubing formed from a zirconium alloy containing 1.0 per cent by weight niobium and produced according to the flow diagram of Figure 1;

Figures 4A, B, C and D show transmission electron microscopy photomicrographs illustrating the typical precipitate distribution and size observed in a fully annealed tubing formed from a zirconium alloy containing 2.5 per cent by weight niobium and produced according to the flow diagram of Figure 1; and

Figures 5A, B, C and D show transmission electron microscopy photomicrographs illustrating the typical precipitate distribution and size observed in a fully annealed tubing formed from a zirconium alloy containing 2.5 per cent by weight niobium and 0.5 per cent by weight copper and produced according to the flow diagram of Figure 1.

Referring to Figure 1, a niobium-containing zirconium alloy (A) ingot, containing 1.0 per cent by weight niobium and the balance zirconium, was conventionally broken down in billets of about 152.4 mm (six inches) in diameter (Step 1). A 152.4 mm (six-inch) diameter billet was then given a beta treatment, Step 2, which comprised holding the billet in a furnace at about 968—996°C (1775—1825°F) for about fifteen minutes and then water quencing the billet. At this point, the beta-treated billet was machined, bore-holed and inspected in preparation for extrusion. The hollow niobium-containing zirconium alloy billet was then heated to about 649°C (1200°F) and extruded (Step 3) to a hollow tube having an outside diameter of 163.5 mm (2.5 inches) and a wall thickness of 10.92 mm (0.43 inch).

The extruded hollow tube was beta-annealed (Step 4) at 954°C (1750°F) for a period of fifteen minutes in preparation for a first cold working step (a pilgering reduction), (Step 5). The beta-annealed extrusion was pilgered in Step 5 to a TREX having an outside diameter of 1.75 inches and a wall thickness of 0.3 inch. The TREX was then annealed, (Step 6), at 500°C (932°F) for a period of 8 hours. Following the annealing of the TREX, the same was then cold pilgered to a tube shell having an outside diameter of 31.75 mm (1.25 inches) and a wall thickness of 4.06 mm (0.16 inch), (Step 7). The tube shell was then further annealed and cold worked according to the following sequence. The tube shell was annealed, (Step 8), at about 524°C (975°F) for 7.5 hours and further cold pilgered, (Step 9) to reduce the tube shell to one having an outside diameter of 22,225 mm (0.875 inch) and a wall thickness of 2.16 mm (0.085 inch). This tube shell was again annealed at about 524°C (975°F) for 7.5 hours, (Step 10). The annealed tube shell was again further cold pilgered, (Step 11), to give a tube shell having an outside diameter of 15.29 mm (0.602 inch) and a wall thickness of 1,14 mm (0.045 inch). A further cold working anneal, (Step 12), was effected at about 524°C (975°F) for 7.5 hours and the tube shell finally cold pilgered, (Step 13), to give a tube having an outside diameter of 10.74 mm (0.423 inch) and a wall thickness of 0.635 mm (0.025 inch). The tube was then subjected to a final anneal at about 427°C (800°F) for 4 hours, (Step 14).

A second niobium-containing alloy (B) ingot, containing 2.5 per cent by weight niobium and the balance zirconium, was treated according to the present process, the B composition ingot treated as was A, except for the following variations. An examination of the TREX indicated that the B composition had not received the correct beta-anneal and was, prior to Step 7, given a futher, extra annealing at 580°C (1076°F) for a period of 8 hours. Also, the cold working anneal for the tubes formed from composition B were effected at about 580°C (1076°F) for 8 hours (rather than 524°C (975°F) for 7.5 hours as with A). The remaining treatment steps, including the final anneal were the same as those used with composition A.

A third niobium-containing alloy (C) ingot, containing 2.5 per cent by weight niobium, 0.5 per cent by weight copper, and the balance zirconium, was treated according to the present invention, the C composition ingot treated as was composition A through Step 5. the TREX was then annealed in Step 6 at 600°C (1112°F) for a period of 8 hours. When the cold working of Step 7 was attempted, transverse cracks appeared. The material was therefore subjected to an additional anneal for 3 hours at about 685°C (1265°F) and the material then subjected to Step 7 with successful pilgering. Also, the first cold working anneal, Step 8, was carried out at about 593°C (1100°F) for a period of 8 hours. Subsequent cold working anneals were effected at about 580°C (1076°F), as with composition B. After the final cold work step, Step 13, the tube was subjected to a final anneal, Step 14, for 7.5 hours at about 480°C (896°F).

Stress-relieved sections of tubing of compositions A, B and C, processed as described above, were corrosion tested in a static autoclave in 427°C, 10.3 MPa steam; and 360°C, 18.7 MPa water; and compared with results of such corrosion testing of Zircaloy-4. The results of the corrosion tests are listed in Table I an demonstrate the zirconium-niobium alloys processed according to the present invention have corrosion resistance superior to that of Zircaloy-4.

TABLE I Static Autoclave Corrosion Data

5 Alloy	360°C			427°C		
	Exposure Time (days)	Weight Gain (mg/dm²)	Corrosion Rate* (mg/dm²/day)	Exposure Time (days)	Weight Gain (mg/dm²)	Corrosion Rate* (mg/dm²/day)
Zr — 1% Nb (A)	448	106.3	0.19	290	310.8	0.98
Zr — 2.5% Nb (B)	672	164.8	0.21	290	403.5	1.28
₁₅ Zr — 2.5% Nb — 0.5% Cu (C)	672	111.8	0.17	290	182.7	0.53
Zircaloy-4	672	391.2	0.57	210	728.8	6.05

^{*} Post-transition rate

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Further evidence of the corrosion resistance of the alloys treated according to the present invention is obtained by comparing the corrosion rates of the tubing of niobium-containing alloy containing 2.5 per cent by weight niobium (alloy B) with published data which characterizes the corrosion rates of 2.5 per cent nlobium-zirconium in the "heat treated" condition as described by J. E. LeSurf in 'The Corrison Behaviour of 2.5 Nb Zirconium Alloy", Applications-Related Phenomenon for Zirconium and Its Alloys, ASTM STP 458, American Society for Testing and Materials, 1969, pp. 286—300. This comparison is presented in Table II.

TABLE II

Post-Transition Rates of Tubing B Versus AECL Heat Treated Sheet (360°C)

40		<u>Material</u>	Post-Transition Corrosion Rate (mg/dm ² /day)
	В		0.21
45	*AE	CL Heat Treated:	
	a)	Quenched + Aged	0.43
50	b)	Quenched + 10% Cold Worked + Aged	0.39
50	c)	Quenched + 20% Cold Worked + Aged	0.13
	d)	Quenched + 30% Cold Worked + Aged	0.08
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* Quenching Temperature = 880°C Aging Treatment = 24 hr @ 500°C

Additional evidence of the superior corrosion resistance of the alloys treated according to the present invention is provided by the post-irradiation examinations performed on cladding of fuel rods. Two experimental Zr-Nb alloys were exposed in the BR—3 pressurized water reactor located in Mol, Belgium, for about seven and one-half months (at power). Five high-power fuel rods were removed and sectioned at

five elevations; one section at the peak power location; two sections at 90% power, above and below the peak power location; and two sections at 50% power near the ends. The minimum, maximum, and mean oxide thicknesses from those five sections are listed in Table III, in comparison with Zircaloy-4:

TABLE III

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Oxide Film Thicknesses Measured on Fuel Rods After BR-3 Cycle 3B Irradiation Test

15	Alloy	Minimum (µm)	Maximum µm)	Mean (µm)
	Zr - 1% Nb (A)	1.962	3.875	3.011
20	Zr - 2.5% Nb (B)	2.210	3.022	2.669
	Zircaloy-4	2.633	4.234	3.658

These examinations indicate that nioblum-containing zirconium alloy tubes of the present invention have in-pile corrosion resistance superior to that of Zircaloy-4. This is a property which, in the past, has been attributed only to "heat treated" 2.5% Nb-zirconium alloys (see "The Effect of Aging and Irradiation on the Corrosion of Zr-2.5 wt% Nb", V. F. Urbanic, J. E. LeSurf and A. B. Johnson, Jr.: Corrosion 31 (1975) 15).

Further evidence of the superiority of the tubing prepared according to the present invention is illustrated in Figure 2 where two groups of corrosion data are presented for a zirconium alloy containing 1 per cent by weight niobium. The first group of data (dash lines: 350, 400 and 450°C) were reported for sheet material which was fabricated via standard Russian processing techniques (see A. A. Kiselev, et al., AECL—1724, 1963). The second group of data (solid lines: 360 and 427°C) were obtained from tubing processed according to the present invention. The superiority of the present tubing is demonstrated by the fact that the same exhibits lowr weight gains at 360 and 427°C than the Russion material does, even though the latter was exposed at lower corrosion temperatures 350 and 400°C respectively.

The present processing provides uniform distribution of very fine precipitate particles in the microstructure of niobium-containing zirconium alloys. The microstructure of the fully annealed tubing is illustrated in Figures 3A, B, C and D for composition "A"; 4A, B, C and D for composition "B"; and 5A, B, C and D for composition "C". Because of the fine particle sizes obtained, transmission electron micrographs (TEM)) were taken. In deformed materials, diffraction effects from gain boundaries an dislocations interfere with particle resolution. Therefore, the study of particle dispersions were carried out on fully annealed, final tubing. The final annealing cycle for A was 8 hours at 500°C (932°F), and for B and C was 8 hours at 600°C (1112°F). Results of the characterization of the particle distribution in the annealed material are given in Table IV as follows:

TABLE IV

Data on Particle Size Distributions In Annealed Product Tubing

55 <i>i</i>	•	Average Diameter	
	Alloy	(Angstroms)	Number Density/cm3
60	A	230 (23 nm)	11 x 10 ¹⁴
	ъ в	420 (42 nm)	12×10^{14}
65	C	450 (45 nm)	8 x 10 ¹⁴

The observed precipitate sizes and number densities represent relatively fine dispersions. This is evident when comparing the same to the average diameter in the range of 3000 Angstroms (300 nm) of particle sizes in a conventionally processed Zircaloy-4 alloy.

Claims

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- 1. A process for fabricating thin-walled tubing having a wall thickness of about 1 mm or less from a zirconium-niobium alloy containing from 1 to 2.5 per cent by weight niobium as homogeneously dispersed finely divided particles and optionally up to 0.5 per cent by weight of copper, iron, molybdenum, nickel, tungsten, vanadium or chromium as a third element, balance, apart from impuritles, zirconium, characterized by beta-treating a zirconium niobium alloy billet containing from 1 to 2.5 per cent by weight niobium; extruding said beta-treated billet at a temperature no higher than 650°C to form a tube shell; further deforming said tube shell by cold working the same in a plurality of cold working sages; annealing said tube shell, between each of said stages of cold working at a temperature below 650°C; and final annealing the resultant tubing at a temperature below 600°C, so as to produce a microstructure of the material having niobium particles of a size below about 800 angstroms (80 nm) homogeneously dispersed therein.
 - 2. A process according to claim 1, characterized in that the zirconium-niobium alloy contains 1 or 2.5 per cent by weight of niobium.
 - 3. A process according to claim 2, characterized in that the annealing of the tube shell is at a temperature of from 500—600°C.
 - 4. A process according to claim 3, characterized in that the annealing of the tube shell is at a temperature of about 524°C for a period of about 7.5 hours.
 - 5. A process according to any of claims 1 to 4, characterized in that the final anneal is at a temperature below 500°C.
 - 6. A process according to claim 5, characterized in that the final anneal is at a temperature of about 427°C for a period of about 4 hours.
 - 7. A process according to any of claims 1 to 6, characterized in that following the extruding and prior to the further deforming, the tube shell is beta-annealed by heating the same at a temperature in the range of 850—1050°C and rapidly cooling the same.
 - 8. A process as claimed in claim 1, characterized in that the zirconium-niobium alloy contains 2.5 per cent by weight niobium and 0.5 per cent by weight copper, and said first anneal is at a temperature of about 480°C for a period of about 7.5 hours.
 - 9. A process as claimed in claims 1 to 8, characterized in that the further deforming of the tube shell is effected in three to five stages.
 - 10. A process as claimed in claim 9, characterized in that the further deforming of the tube shell is by pilgering of the same.

Patentansprüche

- 1. Ein Verfahren zur Herstellung dünnwandiger Röhren mit einer Wandstärke von etwa 1 mm oder weniger, bestehend aus einer Zirkonium-Niobium-Legierung, in der 1 bis 2,5 Gew.-% fein verteilte Niobium-Partikel homogen dispergiert sind und die wahlweise bis zu 0,5 Gew.-% Kupfer, Eisen, Molybdän, Nickel, Wolfram, Vanadium oder Chrom als drittes Element enthält, dadurch gekennzeichnet, dass man einen Barren aus Zirkonium-Niobium-Legierung, die 1 bis 2,5 Gew.-% Niobium enthält, einer Beta-Behandlung unterwirft; diese beta-behandelten Barren bei einer Temperatur von nicht mehr als 650°C extrudiert und eine Rohrhülse bildet; weiter diese Rohrhülse in mehreren Kaltbearbeitungsstufen kaltverformt; wobel zwischen jeder Kaltbearbeitungsstufe die Rohrhülse bei einer Temperatur unter 650°C vergütet wird; und eine Endvergütung der enhaltenen Rohrhülse bei einer Temperatur unter 600°C erfolgt, so dass eine Mikrostruktur des Materials gebildet wird, in dem Niobium-Partikel von unter etwa 800 Anstrôm (80 nm) homogen dispergiert sind.
 - 2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Zirkonium-Niobium-Legierung 1 oder 2,5 Gew.-% Niobium enthält.
 - 3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, dass die Vergütung der Rohrhülse bei einer 5. Temperatur von 500° bis 600°C erfolgt.
 - 4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, dass die Vergütung der Rohrhülse bei einer Temperatur von etwa 524°C übber etwa 7 1/1 Sunden erfolgt.
 - 5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die Endvergütung bei einer Temperatur unter 500°C erfolgt.
 - 6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, dass die Endvergütung bei einer Temperatur von etwa 427°C über etwa 4 Stunden erfolgt.
 - 7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass anschließend an das Extrudieren und vor der weiteren Verformung die Rohrhülse durch Erhitzen bei einer Temperatur im Bereich von 850°C bis 1050°C beta-vergütet und sehr schnell wird.
 - 8. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Zirkonium-Niobium-Legierung 2,5

Gew.-% Niobium und 0,5 Gew.-% Kupfer enthält und dass die erste Vergütung bei einer Temperatur von etwa 480°C über 7,5 Stunden erfolgt.

9. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, dass die weitere Verformung der Rohrhülse in drei bis fünf Stufen erfolgt.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, dass die weitere Verformung der Rohrhülse durch Pilgern erfolgt.

Revendications

- 1. Procédé de fabrication de tubes à paroi mince ayant une épaisseur de paroi d'environ 1 mm ou moins à partir d'un alliage zirconium-niobium contenant de 1 à 2,5 pour cent en poids de niobium sous la forme de particules finement divisées dispersées de manière homogène, et optionellement jusqu'à 0,5 pour cent en poids de cuivre, de fer, de molybdène, de nickel, de tungstène, de vanadium ou de chrome en tant que troisième élément, le complément, à part les impuretés, étant constitué par du zirconium, caractérisé en ce qu'il consiste à soumettre à un traitment bêta une billette d'un alliage zirconium-niobium contenant de 1 à 2,5 pour cent en poids de niobium; à extruder ladite billette soumise au traitement bêta à une température ne dépassant pas 650°C pour former une enveloppe tubulaire; à réaliser un déformation additionnelle de ladite enveloppe tubulaire par le formage à froid de cette dernière au cours d'une multiplicité d'étapes de formage à froid; à recuire ladite enveloppe tubulaire, entre chacune desdites étapes de formage à froid, à une température inférieure à 650°C; et à soumettre le tube résultant à un dernier recuit à une température inférieure à 600°C, de manière à produire une microstructure du matériau présentant des particules de niobium de taille inférieure à environ 800 angströms (80 nm) dispersées de façon homogène dans celle-ci.
 - 2. Procédé selon la revendication 1, caractérisé en ce que l'alliage zirconium-niobium contient 1 ou 2,5 pour cent en poids de niobium.
 - 3. Procédé selon la revendication 2, caractérisé en ce que le recuit de l'enveloppe tubulaire a lieu à une température comprise entre 500 et 600°C.
 - 4. Procédé selon la revendication 3, caractérisé en ce que le recuit de l'enveloppe tubulaire a lieu à une température d'environ 524°C pendant une période d'environ 7,5 heures.
 - 5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que le recuit final a lieu à une température inférieure à 500°C.
 - 6. Procédé selon la revendication 5, caractérisé en ce que le recuit final a lieu à une température d'environ 427°C pendant une période d'environ 4 heures.
 - 7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que, à la suite de l'extrusion et avant la déformation additionnelle, l'enveloppe tubulaire est soumise à un traitment de recuit bêta par chauffage de celle-ci à une température comprise dans une gamme allant de 850 à 1050°C et par son refroldissement rapide.
 - 8. Procédé selon la revendication 1, caractérisé en ce que l'alliage zirconium-niobium contient 2,5 pour cent en poids de niobium et 0,5 pour cent en poids de cuivre, et en ce que le premier recult a lieu à une température d'environ 480°C pendant une période d'environ 7,5 heures.
 - 9. Procédé selon les revendications 1 à 8, caractérisé en ce que la déformation additionnelle de l'enveloppe tubulaire est effectuée en trois à cinq étapes.
 - 10. Procédé selon la revendication 9, caractérisé en ce que la déformaton additionnelle de l'enveloppe tubulaire est obtenue par son laminage à pas de pèlerin.

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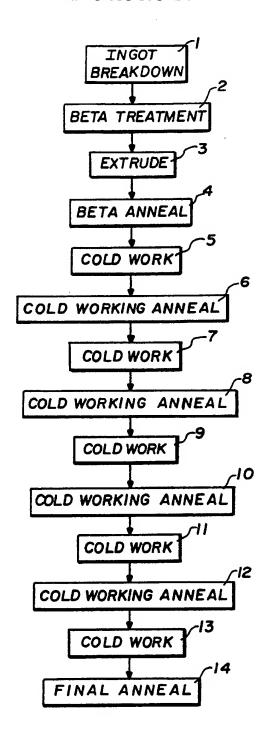
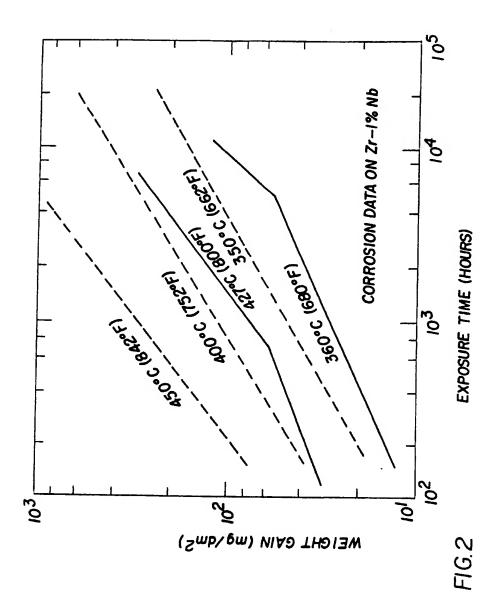
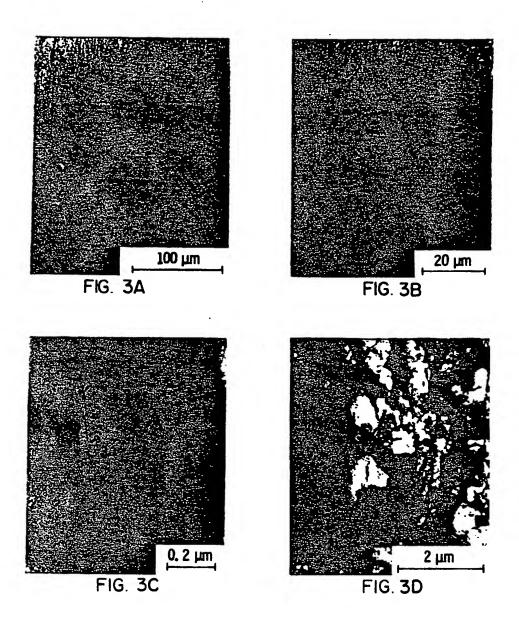
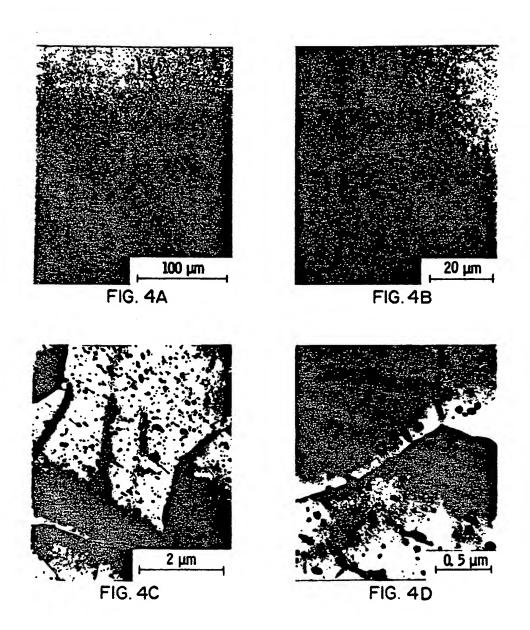
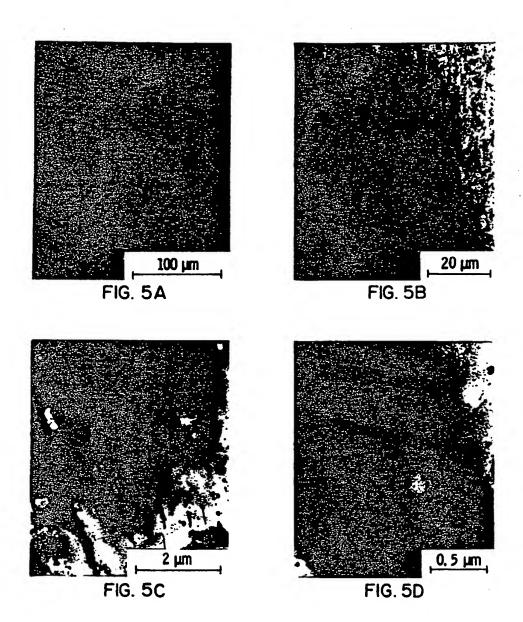


FIG. I









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